

JAPANESE

[JP,2002-155008,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL  
FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE  
DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

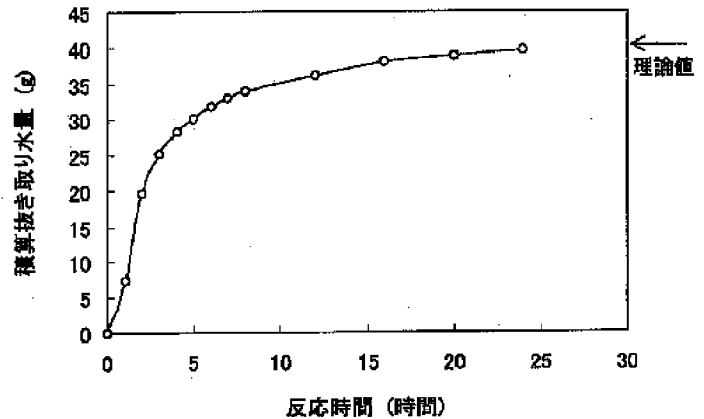
[Field of the Invention]This invention relates to the manufacturing method of the lead screw (beta-diketonate) which is a raw material for forming lead oxide content thin films, such as a capacitor of LSI, by a chemical-vapor-deposition method (CVD method).

[0002]

[Description of the Prior Art]Forming the  $\text{Pb}(\text{Zr}, \text{Ti}) \text{O}_3$  (it expresses the following PZT) film of a ferroelectric with a CVD method to nonvolatile memory is examined. As the lead raw material, the lead screw (dipivaloyl meta-NETO) (it expresses  $\text{Pb}(\text{dpm})_2$  below) in which toxicity volatilizes

low and comparatively easily is leading. This use is expected the high grade thing which contains neither a metallic element impurity nor nonvolatile solid particulates (usually called particle) as much as possible. Since  $\text{Pb}(\text{dpm})_2$  is a solid at a room temperature, particle means here the solid particulates which exist in the state where it melted in

Drawing selection Drawing 1



[Translation done.]

the molten state or solvent of  $\text{Pb}(\text{dpm})_2$ .

[0003]To the manufacturing method of  $\text{Pb}(\text{dpm})_2$ , the next method is publicly known. Below,  $\text{dpmH}$  and a lead screw (acetylacetonate) are expressed as  $\text{Pb}(\text{acac})_2$ , and an acetylacetone is expressed [ lead monoxide ] for  $\text{PbO}$  and dipivaloyl methane as  $\text{acacH}$ .

1. Reaction of reaction 3.  $\text{Pb}(\text{CH}_3\text{COO})_2$  and  $3\text{H}_2\text{O}$  of

reaction 2.  $\text{PbO}$  of  $\text{Pb}$  and  $\text{dpmH}$ , and  $\text{dpmH}$ , and  $\text{Na}(\text{dpm})$

[0004]As an example of 1, in the synthetic example 7 of JP,10-195086,A. It is indicating having added  $\text{dpmH}$  (double mol of  $\text{Pb}$ ) which carried out drying refining, having carried out heating flowing back for 24 hours, having carried out vacuum concentration (100 \*\*, 10Torr) of the reaction mixture subsequently, and having obtained  $\text{Pb}(\text{dpm})_2$ , making the metal  $\text{Pb}$  into suspension into

anhydrous toluene, and stirring it violently. Industrial acquisition is not easy although the  $\text{Pb}$  powder of a high grade is needed for mass-producing  $\text{Pb}(\text{dpm})_2$  of a high grade by this method. Various kinds of impurity metals  $\text{M}$  furthermore contained in  $\text{Pb}$  may react to  $\text{dpmH}$  which is acid, may make  $\text{M}(\text{dpm})_x$ , may form a volatile constituent with  $\text{Pb}(\text{dpm})_2$ , and are not preferred. When a final process is a concentration step, the impurity or particle of the raw material origin or process origin cannot be removed.

[0005]As an example of 2, US No. 5348631 mixes beta-diketone with lead oxide in solvent pentane, and is indicating the method of carrying out reaction promotion with an ultrasonic wave, and manufacturing a lead screw (beta-diketonate). It shall be effective to lead bis(heptafluoro dimethyloctane JIONETO)  $\text{Pb}(\text{fod})_2$  or  $\text{Pb}(\text{dpm})_2$ , and  $\text{Pb}$

( $\text{fod})_2$  is indicated as an example. Although reference is not made in this about processing of the water to generate, water cannot be removed besides the system of reaction with evaporation of pentane during a reaction at least. It is because the boiling point of water is quite higher than pentane.

[0006]R.C. In Mehrotra et al. and "Metal beta-diketonates and applied derivatives" (1978, Academic Press) p28. The method of carrying out heating flowing back of a metallic oxide or metal hydroxide, and the beta-diketone in an inert solvent (benzene and toluene), and compounding metal beta-diketonate, The following examples are indicated that there is the strong point in which output is easily separable from an unreacted oxide or hydroxide when output melts into a solvent, the strong point in which excessive ion is not carried in, and.

$\text{Me}_2\text{SnO} + 2\text{aCaCH} = \text{Me}_2\text{Sn(aCaC)}_2 + \text{H}_2\text{O}$  (flowing back

among benzene)

Reference is not made about processing of the water generated also here.

[0007] As an example of 3, M.A. Malik et al. and Polyhedron Vol.18 (1999) 1641, Na (dpm) which obtained them by making sodium methoxide and dpmH react at a room temperature, It was dropped at the solution of Pb ( $\text{CH}_3\text{COO}$ )<sub>2</sub> and 3H<sub>2</sub>O at the room temperature, and stirred for 1 hour, and filtering separation of the solid substance subsequently generated was carried out, it recrystallized [ hexane ] and the white crystal of Pb(dpm)<sub>2</sub> has been

obtained. However, by this method, a Na compound may carry out ppm order mixing at a product. It is difficult to remove particle thoroughly in a recrystallization process. Therefore, as a process of Pb(dpm)<sub>2</sub> of a high grade, it is not desirable.

[0008]

[Problem(s) to be Solved by the Invention] this technical problem -- the lead screw (beta-diketonate) of a high grade -- a short time -- and it is providing the method of mass-producing with high yield. A high grade means here that each metallic element impurity cannot be found and there is no particle substantially at 0.1 ppm or less.

[0009]

[Means for Solving the Problem] In a method of this invention making lead monoxide and beta-diketone reacting in an organic solvent, and manufacturing a lead screw (beta-diketonate), It is a manufacturing method of a lead screw (beta-diketonate) making it react, removing water to generate one by one besides the system of reaction, distilling off an unreacted material and a solvent subsequently, and carrying out vacuum distillation subsequently. In a method of this invention making lead monoxide and beta-diketone reacting in an organic solvent, and manufacturing a lead screw (beta-diketonate), Do not melt water substantially, but the boiling point is higher than water, and an organic solvent's is lower than beta-diketone, It is a manufacturing method of a lead screw (beta-diketonate) having the process of sampling suitably a water layer which reacted by the boiling state, stored temporarily the reflux having contained water, returned a solvent layer of the upper layer separated with gravity to a reaction vessel, and was divided into a lower layer on the other hand out of a system. This invention is a manufacturing method of a lead screw (beta-diketonate) which a metallic element impurity in a lead screw (beta-diketonate) is 0.1 ppm [ or less ] each, and is characterized by not including particle substantially by the

above-mentioned invention. This invention is a manufacturing method whose lead screw (beta-diketonate) of the above-mentioned invention is a lead screw (dipivaloyl meta-NETO).

[0010]

[Embodiment of the Invention]As (beta-diketonate) of the lead screw (beta-diketonate) in this invention, For example, dipivaloyl meta-NETO (= 2,2,6,6-tetramethyl 3,5-heptane JIONETO), They are 2,6-dimethyl- 3,5-heptane JIONETO, 2,2,6,6-tetramethyl 3,5-octane JIONETO, 2,2,6-trimethyl 3,5-heptane JIONETO, 6-ethyl-2,2-dimethyl- 3,5-octane JIONETO, etc.

[0011]Taking the case of  $\text{Pb(dpm)}_2$ , it explains below. The

reaction in this invention is performed by stirring the slurry of an organic solvent, dpmH, and the fines PbO strongly in an inert atmosphere. Since this reaction is a solid-liquid reaction, it is desirable to improve the fines PbO suspension floating by strong stirring. Therefore, the fines PbO whose pitch diameter is about 50 micrometers or less are used. The charge of dpmH is 2 mol or more to 1 mol of PbO(s).

Required reaction time is about 5 to 50 hours depending on the particle diameter of PbO.

[0012]An easy method is described below most industrially as a method of making it react, removing the water to generate one by one besides the system of reaction. The water produced at the reaction evaporates from a reaction vessel together with the solvent in a boiling state, is cooled by the capacitor, is condensed, and accumulates in a reflux tub. Then, reflux is gravity and a slice is carried out to the upper layer of an organic solvent, and the lower layer of water. Besides by overflow etc., a layer is returned to a reaction vessel. A lower layer is taken out outside suitably and kept from returning to a reaction vessel. Extraction of this water may be continuous or may be intermittent. Since a lower layer will not return to a reaction vessel if a reflux tub is still larger enough, it is not necessary to take out to the last. If the quantity of the water taken out one by one is measured, the percentage of completion of a reaction can be known. The solvent amount of evaporation under reaction should just be an adequate amount that the water to generate can evaporate together with a solvent one by one.

[0013]The organic solvent to be used is not mixed with water, it is higher than water and the boiling point needs to be lower than the raw material dpmH so that such a thing may be possible. Toluene is mentioned as such a solvent. Since toluene often melts  $\text{Pb(dpm)}_2$  of output with 800g /

11 toluene at a room temperature, it is convenient also to recovery of output. In contrast, since octane melts only 150g / 11 octane, it is not preferred.

[0014]After ending reaction, a solvent and unreacted dpmH are removed by distillation and carry out vacuum distillation of the  $\text{Pb(dpm)}_2$  eventually. By carrying out like this, there are few metallic element impurities and high grade  $\text{Pb(dpm)}_2$  without particle is obtained. In neither filtration nor recrystallization, since incorporation of a solvent molecule, remains of high boiling point material, remains of particle, etc. start, it becomes a high grade.

[0015]Since various kinds of metallic element impurities in the raw material PbO exist in the form of an oxide, it is hard to react to dpmH and purification is made by  $\text{Pb(dpm)}_2$

synthesizing process. Since a possibility that an impurity metal will also react to dpmH is large when using the metal Pb for this point and a raw material, it mixes as a metal dpm salt into  $\text{Pb(dpm)}_2$ . Therefore, those who use PbO for a raw material are more convenient than those who use Pb. In order to reduce a metallic element impurity as much as possible furthermore, if the high grade PbO marketed is used as a raw material, the metallic element impurity of Pb (dpm)  $_2$  will be made into 0.1 ppm or less, respectively.

[0016]When it is made to react, removing the water to generate one by one besides the system of reaction, there are the following advantages compared with the case where that is not right.

- (1) Reaction time becomes short.
- (2) Nonvolatile oxide residue is almost lost and yield becomes high.
- (3) Since nonvolatile oxide residue is almost lost, filtration and a decantation process become unnecessary and a process becomes easy.
- (4) The degree of completion of a reaction can be seen by measuring the amount of water to remove.

[0017]It is thought that the side reaction considered that the following  $\text{H}_2\text{O}$  will involve if it is made to react, removing the water to generate one by one besides the system of reaction can be reduced.

Since a lot of dpmH exists in the system of reaction the early stages of a  $\text{Pb(dpm)}_2 + \text{H}_2\text{O} = \text{Pb(dpm)}_2\text{OH} + \text{dpmHPb(dpm)}_2 + \text{H}_2\text{O} = \text{PbO} + 2\text{dpmH}$  reaction. Although the main reaction of  $\text{PbO} + 2\text{dpmH} = \text{Pb(dpm)}_2 + \text{H}_2\text{O}$  advances easily, the concentration of dpmH falls at the telophase of a reaction, and if  $\text{H}_2\text{O}$  exists in a system, it will be thought that it becomes easy to set a side reaction.

[0018]The advantage by carrying out vacuum distillation of the  $\text{Pb(dpm)}_2$  is as follows.

- (1) An impurity metal element decreases.
- (2) lose particle substantially -- \*\*.
- (3) Remove high boiling point material, such as a polymer generated from  $\text{Pb(dpm)}_2$ .

(4) Probably because what has not configured  $\text{H}_2\text{O}$  is obtained, it is hard to deteriorate even if it carries out a mothball.

[0019]

[Example] Vacuum substitution of the manufacture reflux condenser of  $\text{Pb(dpm)}_2$ , a thermometer, and the 51 three-neck flasks provided with stirring wings was carried out, and it was considered as argon atmosphere. Reflux accumulates in the lower part and this reflux condenser has a part, in order to keep reflux from returning to this reaction flask directly.

Collected reflux carries out a slice by gravity, the upper solvent layer overflows and returns to a reaction flask, and the lower layer water layer has structure which can be extracted at any time.

High grade  $\text{PbO}$  504g (2.26 mol) with a mean particle diameter of 25 micrometers, and the toluene 4.01 and  $\text{dpmH}$  1000g (5.43 mol) which was dried were taught, and it heated, stirring violently, and was made the boiling state. Reflux returned the toluene solvent layer of the upper layer overflowed from reflux \*\*\*\*\* of the above-mentioned capacitor to the flask, and lower layer water was sampled suitably and measured. The result of having graph-ized the amount of addition of the water sampled with progress of reaction time is shown in drawing 1. As shown in this figure, 97% of water was extracted for water equivalent to 74% of the amount of theoretical produced water at 5 hours of reactions in 24 hours again.

[0020] Flowing back was stopped in 24 hours, most solvents were distilled off at 1 atmosphere, and, subsequently the remaining solvents, a small amount of water, unreacted  $\text{dpmH}$ , a by-product, etc. were distilled off under reduced pressure. It was the fluid which remained in the flask under heating, and there was neither a solid nor a sediment and it was brown transparent liquid. This liquid was moved to the vacuum unit and 14 g of fore runs and 1238 g of main fractions were obtained at 0.3 Torr and the hot bath temperature of 160-180 \*\* (a main fraction is 2.16 mol as  $\text{Pb(dpm)}_2$ ). 95.6% of yield.

[0021] Solidifying the main fraction at the room temperature, the color was 130 \*\* in melting point in fine light yellow. Under [ a fixed quantity / ICP-MS / Pb content and / impurity / trace element element / it carries out wet degradation of the main fraction and ]. The result is as

follows.

36.0% (36.1% of theoretical value) of Pb content

Impurity (ppm)

Fe<0.1, Cu<0.1, Cr<0.1, nickel<0.1, Co<0.1Mn<0.1,

Mo<0.1, Na<0.1, K< 0.1, Mg<0.1Ca<0.1, U= 0.005,

Th<0.005, each other element <0.1 FD-MS. The

measurement result by the (field desorption ionizing method mass analysis) is shown in [drawing 2](#). The molecular ion

peak was 574 and was a monomer. In a 100 more ml

measuring flask, it dissolved in 97 ml of toluene which dried

4.4 g of main fractions. Although the red laser pointer was

hit against this liquid and visual observation was carried out, there was no particle.

[0022]

[Comparative Example(s)]In the manufacture example of Pb (dpm) <sub>2</sub>, the whole quantity of the reflux from a reflux

condenser was returned to the reaction flask, and also

operation of the same brewing \*\* temperature as an

example and time was performed. Produced water will exist

in a whole-quantity reaction flask. There was a white

sediment in the output of the molten state after distilling off

a solvent etc. Vacuum distillation of this output was carried

out, and 1010 g of light yellow main fractions were obtained

(1.76 mol as Pb(dpm) <sub>2</sub>). 78% of yield. The melting points

of this thing were 130 \*\* and 35.8% of Pb content.

Compared with the example, yield was quite low.

[0023]

[Effect of the Invention]Reaction time becomes short,

nonvolatile oxide residue decreases and yield becomes high

with 95%. Since oxide residue is almost lost, filtration and a

decantation process become unnecessary and a process

becomes easy. Even if an impurity metal element does not

have particle that it is few and substantially with 0.1 ppm

respectively and carries out the mothball of the obtained Pb

(dpm) <sub>2</sub>, it does not deteriorate easily.

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[Translation done.]